

### 3 The First Law: the machinery

#### Solutions to exercises

##### Discussion questions

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**E3.1(b)** The following list includes only those state functions that we have encountered in the first three chapters. More will be encountered in later chapters.

Temperature, pressure, volume, amount, energy, enthalpy, heat capacity, expansion coefficient, isothermal compressibility, and Joule–Thomson coefficient.

**E3.2(b)** One can use the general expression for  $\pi_T$  given in *Justification 3.3* to derive its specific form for a van der Waals gas as given in Exercise 3.14(a), that is,  $\pi_T = a/V_m^2$ . (The derivation is carried out in Example 5.1.) For an isothermal expansion in a van der Waals gas  $dU_m = (a/V_m)^2$ . Hence  $\Delta U_m = -a(1/V_{m,2} - 1/V_{m,1})$ . See this derivation in the solution to Exercise 3.14(a). This formula corresponds to what one would expect for a real gas. As the molecules get closer and closer the molar volume gets smaller and smaller and the energy of attraction gets larger and larger.

**E3.3(b)** The solution to Problem 3.23 shows that the Joule–Thomson coefficient can be expressed in terms of the parameters representing the attractive and repulsive interactions in a real gas. If the attractive forces predominate then expanding the gas will reduce its energy and hence its temperature. This reduction in temperature could continue until the temperature of the gas falls below its condensation point. This is the principle underlying the liquefaction of gases with the Linde Refrigerator which utilizes the Joule–Thomson effect. See Section 3.4 for a more complete discussion.

##### Numerical exercises

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**E3.4(b)** A function has an exact differential if its mixed partial derivatives are equal. That is,  $f(x, y)$  has an exact differential if

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)$$

(a)  $\frac{\partial f}{\partial x} = 3x^2y^2$  and  $\frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right) = 6x^2y$   
 $\frac{\partial f}{\partial y} = 2x^3y$  and  $\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = 6x^2y$  Therefore, exact.

(b)  $\frac{\partial f}{\partial s} = te^s + 1$  and  $\frac{\partial}{\partial t} \left( \frac{\partial f}{\partial s} \right) = e^s$   
 $\frac{\partial f}{\partial t} = 2t + e^s$  and  $\frac{\partial}{\partial s} \left( \frac{\partial f}{\partial t} \right) = e^s$  Therefore, exact.

**E3.5(b)** 
$$dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy = \boxed{\frac{dx}{(1+y)^2} - \frac{2x dy}{(1+y)^3}}$$

**E3.6(b)** (a) 
$$dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy = \boxed{(3x^2 - 2y^2) dx - 4xy dy}$$

(b) 
$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y} (3x^2 - 2y^2) = -4y$$
  
and 
$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x} (-4xy) = -4y$$

$$\mathbf{E3.7(b)} \quad dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy = \boxed{(2xy + y^2) dx + (x^2 + 2xy) dy}$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y} (2xy + y^2) = 2x + 2y$$

$$\text{and } \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x} (x^2 + 2xy) = 2x + 2y$$

$$\mathbf{E3.8(b)} \quad \left( \frac{\partial C_p}{\partial p} \right)_T = \left[ \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial T} \right)_p \right]_T = \frac{\partial^2 H}{\partial p \partial T} \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial p} \right)_T \right]_p$$

Because  $\left( \frac{\partial H}{\partial p} \right)_T = 0$  for a perfect gas, its temperature derivative also equals zero; thus

$$\left( \frac{\partial C_p}{\partial p} \right)_T = 0.$$

$$\mathbf{E3.9(b)} \quad \left( \frac{\partial H}{\partial U} \right)_p = \frac{(\partial H / \partial V)_p}{(\partial U / \partial V)_p} = \frac{\left( \frac{\partial(U+pV)}{\partial V} \right)_p}{(\partial U / \partial V)_p} = \frac{(\partial U / \partial V)_p + p}{(\partial U / \partial V)_p} = \boxed{1 + \frac{p}{(\partial U / \partial V)_p}}$$

$$\mathbf{E3.10(b)} \quad \boxed{dp = \left( \frac{\partial p}{\partial V} \right)_T dV + \left( \frac{\partial p}{\partial T} \right)_V dT}$$

$$d \ln p = \frac{dp}{p} = \frac{1}{p} \left( \frac{\partial p}{\partial V} \right)_T dV + \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V dT$$

We express  $\left( \frac{\partial p}{\partial V} \right)_T$  in terms of the isothermal compressibility  $\kappa_T$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\left[ V \left( \frac{\partial p}{\partial V} \right)_T \right]^{-1} \quad \text{so} \quad \left( \frac{\partial p}{\partial V} \right)_T = -\frac{1}{\kappa_T V}$$

We express  $\left( \frac{\partial p}{\partial T} \right)_V$  in terms of  $\kappa_T$  and the expansion coefficient  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$

$$\left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T = -1 \quad \text{so} \quad \left( \frac{\partial p}{\partial T} \right)_V = -\frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T} = \frac{\alpha}{\kappa_T}$$

$$\text{so } d \ln p = -\frac{1}{pV\kappa_T} + \frac{\alpha}{p\kappa_T} = \boxed{\frac{1}{p\kappa_T} \left( \alpha dT - \frac{dV}{V} \right)}$$

$$\mathbf{E3.11(b)} \quad U = \left( \frac{3}{2} \right) nRT \quad \text{so} \quad \left( \frac{\partial U}{\partial p} \right)_T = \boxed{0} \quad \text{by direct differentiation}$$

$$H = U + pV = \left( \frac{3}{2} \right) nRT + nRT = \left( \frac{5}{2} \right) nRT,$$

$$\text{so } \left( \frac{\partial H}{\partial p} \right)_T = \boxed{0} \quad \text{by direct differentiation}$$

$$\mathbf{E3.12(b)} \quad \alpha = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_p \quad V = \frac{nRT}{p} \quad \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p} = \frac{V}{T}$$

$$\alpha = \left( \frac{1}{V} \right) \times \left( \frac{V}{T} \right) = \boxed{\frac{1}{T}}$$

$$\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T \quad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

$$\kappa_T = -\left(\frac{1}{V}\right) \times \left(-\frac{nRT}{p^2}\right) = \boxed{\frac{1}{p}}$$

**E3.13(b)** The Joule–Thomson coefficient  $\mu$  is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-10 \text{ K}}{(1.00 - 22) \text{ atm}} = \boxed{0.48 \text{ K atm}^{-1}}$$

**E3.14(b)**  $U_m = U_m(T, V_m) \quad dU_m = \left(\frac{\partial U_m}{\partial T}\right)_{V_m} dT + \left(\frac{\partial U_m}{\partial V_m}\right) dV_m$

$dT = 0$  in an isothermal process, so

$$dU_m = \left(\frac{\partial U_m}{\partial V_m}\right)_T dV_m = \frac{a}{V_m^2} dV_m$$

$$\begin{aligned} \Delta U_m &= \int_{V_{m1}}^{V_{m2}} dU_m = \int_{V_{m1}}^{V_{m2}} \frac{a}{V_m^2} dV_m = a \int_{1.00 \text{ L mol}^{-1}}^{22.1 \text{ L mol}^{-1}} \frac{dV_m}{V_m^2} = -\frac{a}{V_m} \Big|_{1.00 \text{ L mol}^{-1}}^{22.1 \text{ L mol}^{-1}} \\ &= -\frac{a}{22.1 \text{ L mol}^{-1}} + \frac{a}{1.00 \text{ L mol}^{-1}} = \frac{21.1a}{22.1 \text{ L mol}^{-1}} = 0.95475a \text{ L}^{-1} \text{ mol} \end{aligned}$$

$$a = 1.337 \text{ atm L}^2 \text{ mol}^{-2}$$

$$\Delta U_m = (0.95475 \text{ mol L}^{-1}) \times (1.337 \text{ atm L}^2 \text{ mol}^{-2})$$

$$= (1.2765 \text{ atm L mol}^{-1}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ L}}\right)$$

$$= 129 \text{ Pa m}^3 \text{ mol}^{-1} = \boxed{129 \text{ J mol}^{-1}}$$

$$w = -\int p_{\text{ex}} dV_m \quad \text{and} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{for a van der Waals gas}$$

$$\text{so } w = -\int \left(\frac{RT}{V_m - b}\right) dV_m + \int \frac{a}{V_m^2} dV_m = -q + \Delta U_m$$

Thus

$$\begin{aligned} q &= +\int_{1.00 \text{ L mol}^{-1}}^{22.1 \text{ L mol}^{-1}} \left(\frac{RT}{V_m - b}\right) dV_m = +RT \ln(V_m - b) \Big|_{1.00 \text{ L mol}^{-1}}^{22.1 \text{ L mol}^{-1}} \\ &= +(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &\quad \times \ln \left\{ \frac{22.1 - 3.20 \times 10^{-2}}{1.00 - 3.20 \times 10^{-2}} \right\} \\ &= \boxed{+7.7465 \text{ kJ mol}^{-1}} \end{aligned}$$

$$w = -7747 \text{ J mol}^{-1} + 129 \text{ J mol}^{-1} = \boxed{-7618 \text{ J mol}^{-1}} = \boxed{-7.62 \text{ kJ mol}^{-1}}$$

**E3.15(b)** The expansion coefficient is

$$\begin{aligned}\alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{V'(3.7 \times 10^{-4} \text{ K}^{-1} + 2 \times 1.52 \times 10^{-6} T \text{ K}^{-2})}{V} \\ &= \frac{V'[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6}(T/\text{K})] \text{ K}^{-1}}{V'[0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2]} \\ &= \frac{[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6}(310)] \text{ K}^{-1}}{0.77 + 3.7 \times 10^{-4}(310) + 1.52 \times 10^{-6}(310)^2} = \boxed{1.27 \times 10^{-3} \text{ K}^{-1}}\end{aligned}$$

**E3.16(b)** Isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \approx -\frac{\Delta V}{V \Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V \kappa_T}$$

A density increase 0.08 per cent means  $\Delta V/V = -0.0008$ . So the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21 \times 10^{-6} \text{ atm}^{-1}} = \boxed{3.6 \times 10^2 \text{ atm}}$$

**E3.17(b)** The isothermal Joule–Thomson coefficient is

$$\left( \frac{\partial H}{\partial p} \right)_T = -\mu C_p = -(1.11 \text{ K atm}^{-1}) \times (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-41.2 \text{ J atm}^{-1} \text{ mol}^{-1}}$$

If this coefficient is constant in an isothermal Joule–Thomson experiment, then the heat which must be supplied to maintain constant temperature is  $\Delta H$  in the following relationship

$$\frac{\Delta H/n}{\Delta p} = -41.2 \text{ J atm}^{-1} \text{ mol}^{-1} \quad \text{so} \quad \Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1})n \Delta p$$

$$\Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (12.0 \text{ mol}) \times (-55 \text{ atm}) = \boxed{27.2 \times 10^3 \text{ J}}$$

**E3.18(b)** The Joule–Thomson coefficient is

$$\mu = \left( \frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p} \quad \text{so} \quad \Delta p = \frac{\Delta T}{\mu} = \frac{-4.5 \text{ K}}{13.3 \times 10^{-3} \text{ K kPa}^{-1}} = \boxed{-3.4 \times 10^2 \text{ kPa}}$$

## Solutions to problems

Assume that all gases are perfect and that all data refer to 298 K unless stated otherwise.

### Solutions to numerical problems

**P3.1**  $\kappa_T = (2.21 \times 10^{-6} \text{ atm}^{-1}) \times \left( \frac{1 \text{ atm}}{1.013 \times 10^5 \text{ Pa}} \right) = \boxed{2.18 \times 10^{-11} \text{ Pa}^{-1}}$

For the change of volume with pressure, we use

$$dV = \left( \frac{\partial V}{\partial p} \right)_T dp[\text{constant temperature}] = -\kappa_T V dp \quad \left[ \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \right]$$

$$\Delta V = -\kappa_T V \Delta p \quad [\text{If change in } V \text{ is small compared to } V]$$

$$\Delta p = (1.03 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (1000 \text{ m}) = 1.01\bar{0} \times 10^7 \text{ Pa.}$$

Consequently, since  $V = 1000 \text{ cm}^3 = 1.0 \times 10^{-3} \text{ m}^3$ ,

$$\begin{aligned}\Delta V &\approx (-2.18 \times 10^{-11} \text{ Pa}^{-1}) \times (1.0 \times 10^{-3} \text{ m}^3) \times (1.010 \times 10^7 \text{ Pa}) \\ &= -2.2 \times 10^{-7} \text{ m}^3, \quad \text{or} \quad \boxed{-0.220 \text{ cm}^3}.\end{aligned}$$

For the change of volume with temperature, we use

$$dV = \left( \frac{\partial V}{\partial T} \right)_p dT [\text{constant pressure}] = \alpha V dT \quad \left[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \right]$$

$$\begin{aligned}\Delta V &\approx \alpha V \Delta T \quad [\text{if change in } V \text{ is small compared to } V] \\ &\approx (8.61 \times 10^{-5} \text{ K}^{-1}) \times (1.0 \times 10^{-3} \text{ m}^3) \times (-30 \text{ K}) \\ &\approx -2.6 \times 10^{-6} \text{ m}^3, \quad \text{or} \quad -2.6 \text{ cm}^3\end{aligned}$$

Overall,  $\Delta V \approx -2.8 \text{ cm}^3$   $\boxed{V = 997.2 \text{ cm}^3}$

**Comment.** A more exact calculation of the change of volume as a result of simultaneous pressure and temperature changes would be based on the relationship

$$dV = \left( \frac{\partial V}{\partial p} \right)_T dp + \left( \frac{\partial V}{\partial T} \right)_p dT = -\kappa_T V dp + \alpha V dT$$

This would require information not given in the problem statement.

### P3.5

Use the formula derived in Problem 3.25.

$$C_{p,m} - C_{V,m} = \lambda R \quad \frac{1}{\lambda} = 1 - \frac{(3V_r - 1)^2}{4V_r^3 T_r}$$

$$\text{which gives } \gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{V,m} + \lambda R}{C_{V,m}} = 1 + \frac{\lambda R}{C_{V,m}}$$

In conjunction with  $C_{V,m} = \frac{3}{2}R$  for a monatomic, perfect gas, this gives

$$\gamma = 1 + \frac{2}{3}\lambda$$

For a van der Waals gas  $V_r = \frac{V_m}{V_c} = \frac{V_m}{3b}$ ,  $T_r = \frac{T}{T_c} = \frac{27RbT}{8a}$  (Table 1.6) with  $a = 4.137 \text{ L}^2 \text{ atm mol}^{-2}$  and  $b = 5.16 \times 10^{-2} \text{ L mol}^{-1}$  (Table 1.6). Hence, at  $100^\circ\text{C}$  and  $1.00 \text{ atm}$ , where  $V_m \approx \frac{RT}{p} = 30.6 \text{ L mol}^{-1}$

$$V_r \approx \frac{30.6 \text{ L mol}^{-1}}{(3) \times (5.16 \times 10^{-2} \text{ L mol}^{-1})} = 198$$

$$T_r \approx \frac{(27) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (5.16 \times 10^{-2} \text{ L mol}^{-1}) \times (373 \text{ K})}{(8) \times (4.137 \text{ L}^2 \text{ atm mol}^{-2})} \approx 1.29$$

Hence

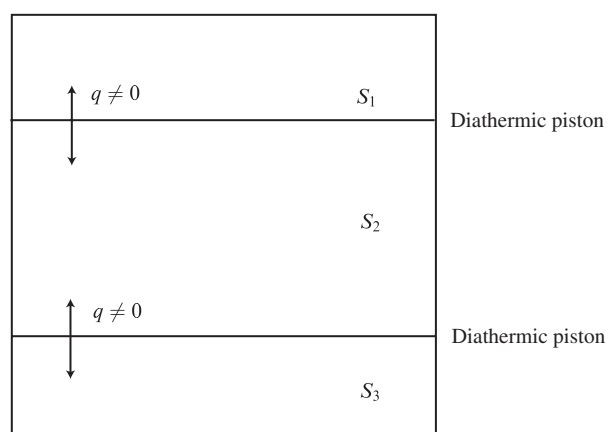
$$\frac{1}{\lambda} = 1 - \frac{[(3) \times (198) - (1)]^2}{(4) \times (198)^3 \times (1.29)} = 1 - 0.0088 = 0.9912, \quad \lambda = 1.009$$

$$\gamma \approx (1) + \left( \frac{2}{3} \right) \times (1.009) = \boxed{1.67}$$

**Comment.** At  $100^\circ\text{C}$  and 1.00 atm xenon is expected to be close to perfect, so it is not surprising that  $\gamma$  differs only slightly from the perfect gas value of  $\frac{5}{3}$ .

**P3.7** See the solution to Problem 3.6. It does not matter whether the piston between chambers 2 and 3 is diathermic or adiabatic as long as the piston between chambers 1 and 2 is adiabatic. The answers are the same as for Problem 3.6. However, if both pistons are diathermic, the result is different. The solution for both pistons being diathermic follows.

See Fig. 3.1.



**Figure 3.1**

*Initial equilibrium state.*

$n = 1.00$  mol diatomic gas in each section

$p_i = 1.00$  bar

$T_i = 298$  K

For each section

$$V_i = \frac{nRT_i}{p_i} = \frac{(1 \text{ mol}) \times (0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1.00 \text{ bar}} = 24.8 \text{ L}$$

$$V_{\text{total}} = 3V_i = 74.3 \text{ L} = \text{constant}$$

*Final equilibrium state.* The diathermic walls allow the passage of heat. Consequently, at equilibrium all chambers will have the same temperature  $T_1 = T_2 = T_3 = 348$  K. The chambers will also be at mechanical equilibrium so

$$\begin{aligned} p_1 = p_2 = p_3 &= \frac{(n_1 + n_2 + n_3)RT_1}{V_{\text{total}}} \\ &= \frac{(3 \text{ mol}) \times (0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (348 \text{ K})}{74.3 \text{ L}} \\ &= 1.17 \text{ bar} = p_2 = p_3 \end{aligned}$$

The chambers will have equal volume.

$$V_1 = \frac{V_{\text{total}}}{3} = V_i = \boxed{24.8 \text{ L} = V_1 = V_2 = V_3}$$

$$\begin{aligned} \Delta U_1 &= n_1 C_V \Delta T_1 = n_1 \left(\frac{5}{2}R\right) \Delta T_1 \\ &= (1 \text{ mol}) \times \left(\frac{5}{2}\right) \times (8.31451 \text{ J K}^{-1} \text{ mol}^{-1}) \times (348 \text{ K} - 298 \text{ K}) \end{aligned}$$

$$\Delta U_1 = 1.04 \text{ kJ} = \Delta U_2 = \Delta U_3$$

$$\Delta U_{\text{total}} = 3\Delta U_1 = 3.12 \text{ kJ} = \Delta U_{\text{total}}$$

### Solutions to theoretical problems

**P3.11**

$$dw = \left(\frac{\partial w}{\partial x}\right)_{y,z} dx + \left(\frac{\partial w}{\partial y}\right)_{x,z} dy + \left(\frac{\partial w}{\partial z}\right)_{x,y} dz$$

$$dw = \boxed{(y+z) dx + (x+z) dy + (x+y) dz}$$

This is the total differential of the function  $w$ , and a total differential is necessarily exact, but here we will demonstrate its exactness showing that its integral is independent of path.

*Path a*

$$dw = 2x dx + 2y dy + 2z dz = 6x dx$$

$$\int_{(0,0,0)}^{(1,1,1)} dw = \int_0^1 6x dx = 3$$

*Path b*

$$dw = 2x^2 dx + (y^{1/2} + y) dy + (z^{1/2} + z) dz = (2x^2 + 2x + 2x^{1/2}) dx$$

$$\int_{(0,0,0)}^{(1,1,1)} dw = \int_0^1 (2x^2 + 2x + 2x^{1/2}) dx = \frac{2}{3} + 1 + \frac{4}{3} = 3$$

Therefore,  $dw$  is exact.

**P3.12**

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

For  $U = \text{constant}$ ,  $dU = 0$ , and

$$C_V dT = -\left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{or} \quad C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

This relationship is essentially the permuter [Relation 3, *Further information 1.7*].

**P3.13**

$$H = H(T, p)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

For  $H = \text{constant}$ ,  $dH = 0$ , and

$$\begin{aligned} \left(\frac{\partial H}{\partial p}\right)_T dp &= -C_p dT \\ \left(\frac{\partial H}{\partial p}\right)_T &= -C_p \left(\frac{dT}{dp}\right)_H = -C_p \left(\frac{\partial T}{\partial p}\right)_H = -C_p \mu = \boxed{-\mu C_p} \end{aligned}$$

This relationship is essentially the permuter [Relation 3, *Further information 1.7*].

- P3.16** The reasoning here is that an exact differential is always exact. If the differential of heat can be shown to be inexact in one instance, then its differential is in general inexact, and heat is not a state function. Consider the cycle shown in Fig. 3.2.

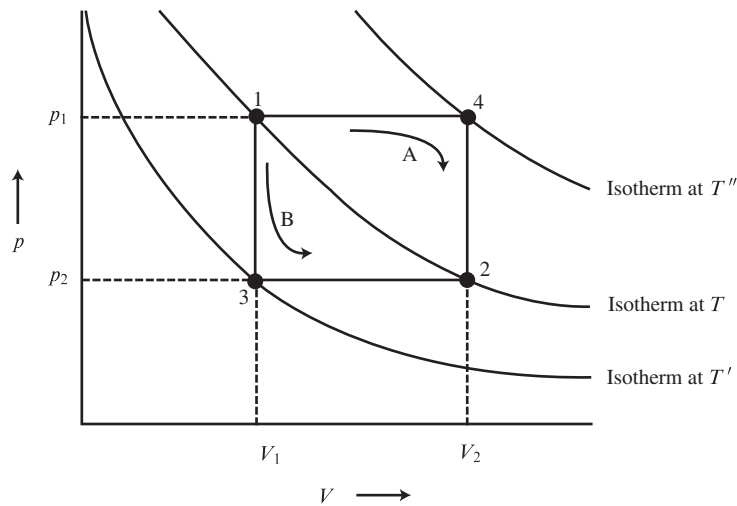


Figure 3.2

The following perfect gas relations apply at points labelled 1, 2, 3 and 4 in Fig. 3.2.

$$(1) p_1 V_1 = p_2 V_2 = nRT, \quad (2) p_2 V_1 = nRT', \quad (3) p_1 V_2 = nRT''$$

Define  $\Delta T' = T - T'$ ,  $\Delta T'' = T'' - T$

Subtract (2) from (1)

$$-nRT' + nRT = -p_2 V_1 + p_1 V_1$$

$$\text{giving } \Delta T' = \frac{V_1(p_1 - p_2)}{RT}$$

Subtracting (1) from (3) we obtain

$$\Delta T'' = \frac{V_2(p_1 - p_2)}{RT}$$

Since  $V_1 \neq V_2$ ,  $\Delta T' \neq \Delta T''$

$$q_A = C_p \Delta T'' - C_V \Delta T'' = (C_p - C_V) \Delta T''$$

$$q_B = -C_V \Delta T' + C_p \Delta T' = (C_p - C_V) \Delta T'$$

giving  $q_A \neq q_B$  and  $q(\text{cycle}) = q_A - q_B \neq 0$ .

Therefore  $\oint dq \neq 0$  and  $dq$  is not exact.

**P3.18**

$$p = p(T, V) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$dp = \left( \frac{\partial p}{\partial T} \right)_V dT + \left( \frac{\partial p}{\partial V} \right)_T dV$$



In what follows adopt the notation  $V_m = V$ .

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\text{then, } dp = \left(\frac{R}{V-b}\right) dT + \left\{\frac{2a}{V^3} - \frac{RT}{(V-b)^2}\right\} dV$$

Because the van der Waals equation is a cubic in  $V$ ,  $\left(\frac{\partial V}{\partial T}\right)_p$  is more readily evaluated with the use of the permuter.

$$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{\frac{R}{V-b}}{\left(-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right)} = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2}$$

For path *a*

$$\begin{aligned} \int_{T_1, V_1}^{T_2, V_2} dp &= \int_{T_1}^{T_2} \frac{R}{V_1-b} dT + \int_{V_1}^{V_2} \left[-\frac{RT_2}{(V-b)^2} + \frac{2a}{V^3}\right] dV \\ &= \frac{R}{V_1-b}(T_2 - T_1) + \frac{RT_2}{(V_2-b)} - \frac{RT_2}{(V_1-b)} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) \\ &= -\frac{RT_1}{V_1-b} + \frac{RT_2}{V_2-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) \end{aligned}$$

For path *b*

$$\begin{aligned} \int_{T_1, V_1}^{T_2, V_2} dp &= \int_{V_1}^{V_2} \left[-\frac{RT_1}{(V-b)^2} + \frac{2a}{V^3}\right] dV + \int_{T_1}^{T_2} \frac{R}{V_2-b} dT \\ &= \frac{RT_1}{V_2-b} - \frac{RT_1}{V_1-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \frac{R}{V_2-b}(T_2 - T_1) \\ &= -\frac{RT_1}{V_1-b} + \frac{RT_2}{V_2-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) \end{aligned}$$

Thus, they are the same and  $dp$  satisfies the condition of an exact differential, namely, that its integral between limits is independent of path.

### P3.20

$$p = p(V, T)$$

Therefore,

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \quad \text{with } p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \text{ [Table 1.6]}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{-nRT}{(V-nb)^2} + \frac{2n^2a}{V^3} = \frac{-p}{V-nb} + \left(\frac{n^2a}{V^3}\right) \times \left(\frac{V-2nb}{V-nb}\right)$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb} = \frac{p}{T} + \frac{n^2a}{TV^2}$$

Therefore, upon substitution

$$\begin{aligned} dp &= \left( \frac{-p dV}{V-nb} \right) + \left( \frac{n^2 a}{V^3} \right) \times (V-2nb) \times \left( \frac{dV}{V-nb} \right) + \left( \frac{p dT}{T} \right) + \left( \frac{n^2 a}{V^2} \right) \times \left( \frac{dT}{T} \right) \\ &= \left( \frac{(n^2 a) \times (V-nb)/V^3 - p}{V-nb} \right) dV + \left( \frac{p + n^2 a/V^2}{T} \right) dT \\ &= \boxed{\left( \frac{a(V_m - b)/V_m^3 - p}{V_m - b} \right) dV_m + \left( \frac{p + a/V_m^2}{T} \right) dT} \end{aligned}$$

**Comment.** This result may be compared to the expression for  $dp$  obtained in Problem 3.18.

**P3.21**

$$p = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \quad (\text{Table 1.6})$$

$$\text{Hence } T = \boxed{\left( \frac{p}{nR} \right) \times (V-nb) + \left( \frac{na}{RV^2} \right) \times (V-nb)}$$

$$\boxed{\left( \frac{\partial T}{\partial p} \right)_V = \frac{V-nb}{nR}} = \frac{V_m - b}{R} = \frac{1}{\left( \frac{\partial p}{\partial T} \right)_V}$$

For Euler's chain relation, we need to show that  $\left( \frac{\partial T}{\partial p} \right)_V \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p = -1$

Hence, in addition to  $\left( \frac{\partial T}{\partial p} \right)_V$  and  $\left( \frac{\partial p}{\partial V} \right)_T$  [Problem 3.20] we need  $\left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{\left( \frac{\partial T}{\partial V} \right)_p}$

$$\begin{aligned} \text{which can be found from } \left( \frac{\partial T}{\partial V} \right)_p &= \left( \frac{p}{nR} \right) + \left( \frac{na}{RV^2} \right) - \left( \frac{2na}{RV^3} \right) \times (V-nb) \\ &= \left( \frac{T}{V-nb} \right) - \left( \frac{2na}{RV^3} \right) \times (V-nb) \end{aligned}$$

Therefore,

$$\begin{aligned} \left( \frac{\partial T}{\partial p} \right)_V \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p &= \frac{\left( \frac{\partial T}{\partial p} \right)_V \left( \frac{\partial p}{\partial V} \right)_T}{\left( \frac{\partial T}{\partial V} \right)_p} \\ &= \frac{\left( \frac{V-nb}{nR} \right) \times \left( \frac{-nRT}{(V-nb)^2} + \frac{2n^2 a}{V^3} \right)}{\left( \frac{T}{V-nb} \right) - \left( \frac{2na}{RV^3} \right) \times (V-nb)} = \frac{\left( \frac{-T}{V-nb} \right) + \left( \frac{2na}{RV^3} \right) \times (V-nb)}{\left( \frac{T}{V-nb} \right) - \left( \frac{2na}{RV^3} \right) \times (V-nb)} \\ &= -1 \end{aligned}$$

**P3.23**

$$\mu C_p = T \left( \frac{\partial V}{\partial T} \right)_p - V = \frac{T}{\left( \frac{\partial T}{\partial V} \right)_p} - V \quad [\text{Relation 2, Further information 1.7}]$$

$$\left( \frac{\partial T}{\partial V} \right)_p = \frac{T}{V-nb} - \frac{2na}{RV^3} (V-nb) \quad [\text{Problem 3.21}]$$

Introduction of this expression followed by rearrangement leads to

$$\mu C_p = \frac{(2na) \times (V - nb)^2 - nbRTV^2}{RTV^3 - 2na(V - nb)^2} \times V$$

Then, introducing  $\zeta = \frac{RTV^3}{2na(V - nb)^2}$  to simplify the appearance of the expression

$$\boxed{\mu C_p = \left( \frac{1 - \frac{nb\zeta}{V}}{\zeta - 1} \right) V = \left( \frac{1 - \frac{b\zeta}{V_m}}{\zeta - 1} \right) V}$$

For xenon,  $V_m = 24.6 \text{ L mol}^{-1}$ ,  $T = 298 \text{ K}$ ,  $a = 4.137 \text{ L}^2 \text{ atm mol}^{-2}$ ,  $b = 5.16 \times 10^{-2} \text{ L mol}^{-1}$ ,

$$\frac{nb}{V} = \frac{b}{V_m} = \frac{5.16 \times 10^{-2} \text{ L mol}^{-1}}{24.6 \text{ L mol}^{-1}} = 2.09 \times 10^{-3}$$

$$\zeta = \frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (24.6 \text{ L mol}^{-1})^3}{(2) \times (4.137 \text{ L}^2 \text{ atm mol}^{-2}) \times (24.6 \text{ L mol}^{-1} - 5.16 \times 10^{-2} \text{ L mol}^{-1})^2} = 73.0$$

Therefore,  $\mu C_p = \frac{1 - (73.0) \times (2.09 \times 10^{-3})}{72.0} \times (24.6 \text{ L mol}^{-1}) = 0.290 \text{ L mol}^{-1}$

$C_p = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$  [Table 2.6], so

$$\begin{aligned} \mu &= \frac{0.290 \text{ L mol}^{-1}}{20.79 \text{ J K}^{-1} \text{ mol}^{-1}} = \frac{0.290 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}}{20.79 \text{ J K}^{-1} \text{ mol}^{-1}} \\ &= 1.39\bar{3} \times 10^{-5} \text{ K m}^3 \text{ J}^{-1} = 1.39\bar{3} \times 10^{-5} \text{ K Pa}^{-1} \\ &= (1.39\bar{3} \times 10^{-5}) \times (1.013 \times 10^5 \text{ K atm}^{-1}) = \boxed{1.41 \text{ K atm}^{-1}} \end{aligned}$$

The value of  $\mu$  changes at  $T = T_1$  and when the sign of the numerator  $1 - \frac{nb\zeta}{V}$  changes sign ( $\zeta - 1$  is positive). Hence

$$\frac{b\zeta}{V_m} = 1 \text{ at } T = T_1 \quad \text{or} \quad \frac{RT_1 b V^3}{2na(V - nb)^2 V_m} = 1 \quad \text{implying that } T_1 = \frac{2a(V_m - b)^2}{RbV_m^2}$$

$$\text{that is, } T_1 = \left( \frac{2a}{Rb} \right) \times \left( 1 - \frac{b}{V_m} \right)^2 = \boxed{\frac{27}{4} T_c \left( 1 - \frac{b}{V_m} \right)^2}$$

For xenon,  $\frac{2a}{Rb} = \frac{(2) \times (4.137 \text{ L}^2 \text{ atm mol}^{-2})}{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (5.16 \times 10^{-2} \text{ L mol}^{-1})} = 1954 \text{ K}$

and so  $T_1 = (1954 \text{ K}) \times \left( 1 - \frac{5.16 \times 10^{-2}}{24.6} \right)^2 = \boxed{1946 \text{ K}}$

**Question.** An approximate relationship for  $\mu$  of a van der Waals gas was obtained in Problem 3.17. Use it to obtain an expression for the inversion temperature, calculate it for xenon, and compare to the result above.

**P3.25**  $C_{p,m} - C_{V,m} = \frac{\alpha^2 TV}{\kappa_T}$  [3.21]  $= \alpha TV \left( \frac{\partial p}{\partial T} \right)_V$  [Justification 3.3]

$$\left( \frac{\partial p}{\partial T} \right)_V = \frac{nR}{V - nb}$$
 [Problem 3.20]

$$\alpha V = \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{\left( \frac{\partial T}{\partial V} \right)_p}$$

Substituting,

$$C_{p,m} - C_{V,m} = \frac{T \left( \frac{\partial p}{\partial T} \right)_V}{\left( \frac{\partial T}{\partial V} \right)_p} \quad \text{so} \quad \left( \frac{\partial T}{\partial V} \right)_p = \frac{T}{V - nb} - \frac{2na}{RV^3} (V - nb)$$
 [Problem 3.21]

Substituting,

$$C_{p,m} - C_{V,m} = \frac{\frac{nRT}{(V-nb)}}{\frac{T}{(V-nb)} - \left( \frac{2na}{RV^3} \right) \times (V - nb)} = n\lambda R \quad \text{with} \quad \lambda = \frac{1}{1 - \left( \frac{2na}{RTV^3} \right) \times (V - nb)^2}$$

For molar quantities,

$$C_{p,m} - C_{V,m} = \lambda R \quad \text{with} \quad \frac{1}{\lambda} = 1 - \frac{2a(V_m - b)^2}{RTV_m^3}$$

Now introduce the reduced variables and use  $T_c = \frac{8a}{27Rb}$ ,  $V_c = 3b$ .

After rearrangement,

$$\boxed{\frac{1}{\lambda} = 1 - \frac{(3V_r - 1)^2}{4T_r V_r^3}}$$

For xenon,  $V_c = 118.1 \text{ cm}^3 \text{ mol}^{-1}$ ,  $T_c = 289.8 \text{ K}$ . The perfect gas value for  $V_m$  may be used as any error introduced by this approximation occurs only in the correction term for  $\frac{1}{\lambda}$ .

Hence,  $V_m \approx 2.45 \text{ L mol}^{-1}$ ,  $V_c = 118.8 \text{ cm}^3 \text{ mol}^{-1}$ ,  $T_c = 289.8 \text{ K}$ , and  $V_r = 20.6$  and  $T_r = 1.03$ ; therefore

$$\frac{1}{\lambda} = 1 - \frac{(61.8 - 1)^2}{(4) \times (1.03) \times (20.6)^3} = 0.90, \quad \text{giving} \quad \lambda \approx 1.1$$

and

$$C_{p,m} - C_{V,m} \approx 1.1R = \boxed{9.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

**P3.27** (a)  $\mu = -\frac{1}{C_p} \left( \frac{\partial H}{\partial p} \right)_T = \frac{1}{C_p} \left\{ T \left( \frac{\partial V_m}{\partial T} \right)_p - V_m \right\}$  [Justification 3.1 and Problem 3.24]

$$V_m = \frac{RT}{p} + aT^2$$

$$\left( \frac{\partial V_m}{\partial T} \right)_p = \frac{R}{p} + 2aT$$

$$\mu = \frac{1}{C_p} \left\{ \frac{RT}{p} + 2aT^2 - \frac{RT}{p} - aT^2 \right\}$$

$$\boxed{\mu = \frac{aT^2}{C_p}}$$

$$\begin{aligned} \text{(b)} \quad C_V &= C_p - \alpha T V_m \left( \frac{\partial p}{\partial T} \right)_V \\ &= C_p - T \left( \frac{\partial V_m}{\partial T} \right)_p \left( \frac{\partial p}{\partial T} \right)_V \end{aligned}$$

$$\begin{aligned} \text{But, } p &= \frac{RT}{V_m - aT^2} \\ \left( \frac{\partial p}{\partial T} \right)_V &= \frac{R}{V_m - aT^2} - \frac{RT(-2aT)}{(V_m - aT^2)^2} \\ &= \frac{R}{(RT/p)} + \frac{2aRT^2}{(RT/p)^2} \\ &= \frac{p}{T} + \frac{2ap^2}{R} \end{aligned}$$

Therefore

$$\begin{aligned} C_V &= C_p - T \left( \frac{R}{p} + 2aT \right) \times \left( \frac{p}{T} + \frac{2ap^2}{R} \right) \\ &= C_p - \frac{RT}{p} \left( 1 + \frac{2apT}{R} \right) \times \left( 1 + \frac{2apT}{R} \right) \times \left( \frac{p}{T} \right) \end{aligned}$$

$$\boxed{C_V = C_p - R \left( 1 + \frac{2apT}{R} \right)^2}$$

### Solutions to additional problems

#### P3.29

(a) The Joule–Thomson coefficient is related to the given data by

$$\begin{aligned} \mu &= -(1/C_p)(\partial H/\partial p)_T = -(-3.29 \times 10^3 \text{ J mol}^{-1} \text{ MPa}^{-1})/(110.0 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{29.9 \text{ K MPa}^{-1}} \end{aligned}$$

(b) The Joule–Thomson coefficient is defined as

$$\mu = (\partial T/\partial p)_H \approx (\Delta T/\Delta p)_H$$

Assuming that the expansion is a Joule–Thomson constant-enthalpy process, we have

$$\Delta T = \mu \Delta p = (29.9 \text{ K MPa}^{-1}) \times [(0.5 - 1.5) \times 10^{-1} \text{ MPa}] = \boxed{-2.99 \text{ K}}$$